

Universality in Dynamic Coarsening of a Fractal Cluster

Baruch Meerson and Pavel V. Sasorov*

The Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Dynamics of coarsening of a statistically homogeneous fractal cluster, created by morphological instability of growth during an early stage of a first order phase transition, is investigated theoretically. An exact mathematical setting of the problem, obeying a global conservation law, is presented. A statistical mean field theory is developed that accounts for shadowing and assumes that the fractal dimension of the cluster is invariant in time. The coarsening dynamics are found to be self-similar, and the corresponding dynamic scaling exponents are calculated for any Euclidean dimension.

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A non-equilibrium dissipative system undergoes relaxation to equilibrium after the driving agent is “switched off” or depleted. In complex systems the relaxation dynamics can be quite complicated, and it is natural to seek for the dynamic scaling and universality. An instructive, exactly solvable example of dynamic scaling in relaxation (coarsening) of rough surfaces with nonconservative dynamics is given by the deterministic (undriven) KPZ-equation [1,2]. A much older example is decay of homogeneous and isotropic hydrodynamic turbulence [3,4]. Finally, there is an important class of relaxation problems related to phase ordering dynamics, non-conserved and conserved, in the bulk [5–7] and on the surface [8].

In the case of conserved dynamics, “switching off” of the driving agent occurs naturally as a result of a global conservation law. There is an important class of non-equilibrium systems that exhibit strong morphological instabilities and ramified growth at an early stage of the dynamics, show phase ordering at an intermediate stage, and finally approach a simple thermodynamic equilibrium. Examples are provided by realistic diffusion-controlled growth systems, such as deposition of solute from a supersaturated solution and solidification from an overcooled liquid. The stage of morphological instability and its implications has been under extensive investigation [9–13]. On the contrary, the (usually much longer) phase-ordering stage has not been addressed. We claim in this Letter that this generic phase-ordering stage exhibits intrinsic self-similarity, calculate the scaling exponents for any Euclidean dimension $d > 1$ and make predictions that can be tested in experiment or numerical simulations.

We will concentrate, for concreteness, on the problem of growth of a single nucleus (we will call it cluster) from a supersaturated solution and start with a minimalistic

mathematical setting that describes correctly the whole dynamics, from the stage of growth to the final equilibrium. Let $u(\mathbf{r}, t)$ be the mass concentration of the solution normalized to the (constant) density of solute in the compact solid phase. The field u is governed by the diffusion equation

$$\frac{\partial u}{\partial t} = D \nabla^2 u \quad (1)$$

in a finite d -dimensional domain. We specify a no-flux boundary condition,

$$\nabla_n u|_{\Gamma} = 0 \quad (2)$$

on the external boundary Γ , where index n stands for the normal component of a vector. Assuming that the moving interphase boundary γ is in local thermodynamic equilibrium, we employ the Gibbs-Thomson relation

$$u|_{\gamma} = u_0(1 + \lambda_0 \kappa), \quad (3)$$

where u_0 is the (normalized) equilibrium concentration of the solution in the bulk, λ_0 is the capillary length and κ is the local curvature for $d = 2$, or the mean curvature for $d > 2$. (For simplicity, we will limit ourselves to an isotropic surface tension.) Finally, mass conservation at the moving boundary yields the well-known relation for the normal speed:

$$v_n = \frac{D \nabla_n u}{1 - u}|_{\gamma}. \quad (4)$$

It is easy to check that Eqs. (1)–(4) preserve the total mass of the solute. In the normalized form

$$\Omega_c + \int_{\Omega} u d\mathbf{r} = \text{const}, \quad (5)$$

where Ω_c is the volume (area) of the cluster, while Ω denotes the region unoccupied by the cluster. This simple conservation law describes the depletion of solution during the deposition process and imposes an important constraint on the dynamics. This constraint does not appear in the more traditional formulations of the diffusion-controlled growth problem [9–13], where an infinite system is studied, and the boundary condition corresponding to a constant (positive) flux or constant supersaturation at $\mathbf{r} \rightarrow \infty$ is used instead of Eq. (2). Notice that, even in the limit of strong diffusion, it is the full diffusion equation (rather than its Laplace’s equation limit) and no-flux condition on Γ that provide the conservation law. Also, the usually small term u in the denominator of Eq. (4) should be kept to get Eq. (5) right.

Despite a simple formulation, the moving boundary problem (1)-(4) is formidable. In the remainder of this Letter we will present a mean field theory of coarsening that exploits a strong resemblance of this problem to the classical problem of Ostwald ripening [5–7], accounts for shadowing and is based on the assumption that the fractal dimension of the coarsening cluster remains constant on an interval of scales shrinking with time [14,15].

In a sufficiently large and “noisy” system (1)-(4) with small initial supersaturation, a fundamental morphological instability [16] leads to ramification of the moving interface, so that the interface becomes fractal (DLA-like) [13]. Because of mass conservation, the supersaturation decreases with time. Correspondingly, the surface-tension effects mitigate and finally switch off the morphological instability. The coarsening stage is characterized by the (properly scaled down) supersaturation becoming comparable to the mean curvature of the interface. The total cluster mass asymptotically approaches a constant value M_0 , and the main effect at this stage is the diffusion-controlled mass transfer between different branches of the cluster that, in view of Eq. (3), promotes growth of larger branches (that is, those with a smaller curvature) at the expense of smaller ones (those with a larger curvature). This dynamics strongly resembles Ostwald ripening (OR) [5–7]. The classical problem of OR deals with statistics of many separate “drops” of the new phase, and the corresponding statistical mean-field theory [17] assumes a negligibly small volume (or area) fraction of the drops, and completely ignores spatial correlations. It is very important that the dynamic scaling exponent predicted by the mean-field theory [17] agrees very well with experiments and simulations performed under conditions of a finite, or even *large* volume (area) fraction [5,6,8] and significant spatial correlations (even when description in terms of individual drops becomes irrelevant [7]). Inspired by this success, we propose a mean-field theory of coarsening for a statistically homogeneous fractal cluster (that is a cluster whose fractal dimension is constant in space).

Assuming for simplicity, that the cluster is (statistically) azimuthally (for $d = 2$), or spherically (for $d = 3$) symmetric, we introduce a time-dependent distribution function $f(R, r, t)$ for the number of branches with size R situated at the radius r from the cluster center. Looking for self-similarity, we assume a single scaling in R (which implies, in particular, that the typical branch size scales like its curvature radius) and a single scaling in r for the whole cluster. An additional variable is an effective (coarse-grained) supersaturation field $\Delta u(r, t) = u(r, t) - u_0$. The r -dependence in the functions f and Δu accounts for shadowing and, as we will see later, for shrinkage of the coarsening cluster. This dependence has no analog in the “conventional” mean-field theory of OR [17].

Neglecting direct coalescence of branches, we write

down a continuity equation

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial R} (V_R f) = 0, \quad (6)$$

while for V_R we adopt the well-known relation [17,18]

$$V_R = \frac{1}{R} \left(\Delta u - \frac{d-1}{R} \right), \quad (7)$$

following from the solution of an idealized problem of the Laplacian growth of an isolated *spherical* particle with the boundary condition (3) on its interface (all dimensional coefficients are scaled down). Actually, the precise form of Eq. (7) is unessential for our purposes. What is really important (and used in the following) is that the characteristic normal speed of the boundary (that is, expansion/contraction rate of an individual branch) scales like R^{-2} , while the effective supersaturation scales like the characteristic mean curvature (see below).

Introduce the (time-dependent) mass content of the cluster within the radius r :

$$M(r, t) = \frac{d\pi^d}{[\Gamma(\frac{d}{2} + 1)]^2} \int_0^r dr r^{d-1} \int_0^\infty dR R^d f(R, r, t), \quad (8)$$

where $\Gamma(x)$ is the gamma-function. Mass conservation of the coarsening cluster implies that $M(r_c, t) = M_0 = \text{const}$, where r_c is the (time-dependent) cluster radius.

We are looking for self-similarity:

$$f(R, r, t) = t^{-\mu} \Phi(Rt^{-\nu}, rt^\beta), \quad \Delta u(r, t) = t^{-\alpha} U(rt^\beta). \quad (9)$$

Correspondingly, the cluster radius will scale like $r_c(t) = \eta_0 t^{-\beta}$, where η_0 is a constant depending on d . Notice, that the ansatz for f assumes self-similarity with respect to each of the *two* arguments, R and r . Upon substitution, Eqs. (6) and (7) yield

$$\alpha = \nu = 1/3 \quad (10)$$

independently of the Euclidean dimension d and of (still undetermined) β and μ . Employing the mass conservation, we obtain a relation between β and μ :

$$d\beta + \mu - \frac{d+1}{3} = 0. \quad (11)$$

Now we will use the assumption of invariance of the fractal dimension d_f [on an interval of scales $[l_{\min}(t), l_{\max}(t)]$ that is shrinking with time]. It is convenient to work with the mass density of the cluster:

$$\rho(r, t) = \frac{\Gamma(\frac{d}{2} + 1)}{d\pi^{d/2} r^{d-1}} \frac{\partial M(r, t)}{\partial r} = \frac{\pi^{d/2} t^{\frac{d+1}{3}-\mu}}{\Gamma(\frac{d}{2} + 1)} \int_0^\infty d\xi \xi^d \Phi(\xi, \eta), \quad (12)$$

where $\eta = rt^\beta$.

For a (statistically self-similar) “mass fractal” with the fractal dimension d_f one has $M(r, t) = A(t)r^{d_f}$ which implies a density

$$\rho(r, t) \sim A(t)r^{d_f-d} \sim A(t)t^{\beta(d-d_f)}\eta^{d_f-d}. \quad (13)$$

[Since the *coefficients* of the scaling laws (and even the shape functions Φ and U) will remain undetermined, we have omitted here and in the following all d - and d_f -dependent coefficients.] A direct comparison of Eqs. (12) and (13) yields

$$A(t) \sim t^{\frac{d+1}{3}-\mu+\beta(d_f-d)} \quad \text{and} \quad \int_0^\infty d\xi \xi^d \Phi(\xi, \eta) \sim \eta^{d_f-d}. \quad (14)$$

At scales smaller than $l_{min}(t)$ the cluster is already compact. It is natural to identify $l_{min}(t)$ with a typical (for example, mean) value of the branch size $\bar{R}(t)$ that, according to Eq. (10), scales with time like $t^{1/3}$ [19]. Therefore, at radii $r < \bar{R}(t)$ the mass density must be constant. On the other hand, Eqs. (13) and (14) predict the following behavior of the mass density at $r = \bar{R}(t)$:

$$\rho(\bar{R}, t) \sim t^{\frac{d+1}{3}-\mu}(\bar{R}t^\beta)^{d_f-d} \sim t^{-(d-d_f)\beta-\mu+\frac{d_f+1}{3}}.$$

Requiring this to be constant, we have

$$(d-d_f)\beta + \mu - \frac{d_f+1}{3} = 0. \quad (15)$$

Combining Eqs. (11) and (15) we find

$$\beta = \frac{d-d_f}{3d_f}, \quad \mu = \frac{2d+1}{3} - \frac{d^2}{3d_f}. \quad (16)$$

One can see that $\beta > 0$ for any d , so the coarsening cluster is indeed shrinking with time [20]. Also, $\mu > 0$ for any d . Having found the dynamic scaling exponents α, β, μ and ν , we can make a number of predictions. A “global” prediction concerns scaling of the cluster perimeter (for $d = 2$) or interface area (for $d = 3$). These quantities decrease like $t^{-1/3}$ (independently of d and d_f !). Another “global” prediction concerns the already mentioned scaling of the cluster radius: $r_c \sim t^{-(d-d_f)/3d_f}$. For example, for a DLA-like cluster ($d_f \simeq 1.71$ for $d = 2$, and $d_f \simeq 2.5$ for $d = 3$), our predictions are $r_c \sim t^{-0.057}$ and $t^{-0.067}$, respectively. Returning to Eq. (12), we see that the mass density $\rho(r, t) \sim t^\sigma r^{d_f-d}$, where $\sigma = (d-d_f)/3$. For $d = 2$ and 3 we get $\sigma \simeq 0.10$ and 0.17 , respectively.

Self-similar phase-ordering dynamics of a fractal cluster that we have considered crosses over to a compact relaxation dynamics on a time scale t_* for which $l_{min}(t_*) \sim l_{max}(t_*)$, that is $\bar{R}(t_*) \sim r_c(t_*)$. Finally, the cluster acquires spherical (circular) shape, corresponding to the only possible two-phase equilibrium in the system [21].

Our mean-field theory is based on the assumption of a statistically homogeneous cluster. It is well known that the diffusion-controlled fractal growth crosses over to a compact growth when the growing cluster reaches the “diffusion length” [13]. Our estimates show that, for a sufficiently large system and small initial supersaturation, the depletion effects become important before the cluster radius has a chance to reach the diffusion length. As the result, the cluster stops growing and the coarsening effects that we have described starts dominating.

A number of refinements of the theory are straightforward (like an account for growth anisotropy by introducing an additional, angle-dependent factor in the mean-field variables f and Δu). What is probably more important is that similar mean-field theories can be developed for other transport mechanisms (for example, interface-controlled coarsening, see, *e.g.* [8]). The main difference will be in the value of exponent ν , and scaling arguments yield $\nu = 1/2$ in this limit. In addition, we must put $U(\eta) = \text{const}$, as the supersaturation field is uniform in this case [22]. Once ν is found, the rest of exponents can be easily calculated. For the *general* ν , one obtains

$$\beta = \frac{\nu(d-d_f)}{d_f}, \quad \mu = \nu \left(2d+1 - \frac{d^2}{d_f} \right).$$

Correspondingly, the interface area (perimeter in 2d) will decrease like $t^{-\nu}$ independently of d and d_f .

Predictions of the mean-field theory can be checked in experiment and numerical simulations. Simulations are possible with different types of models. For the diffusion-controlled coarsening, one option is the sharp-interface model (1)-(4). Another can employ a conserved phase-field model [7,23]. As noise is not important at the coarsening stage, one can use the noiseless version of any of these two models and start directly from a fractal cluster [24]. One more alternative would be to employ a modified DLA algorithm with the surface tension [25] and total mass conservation properly taken into account. The simulations can be time-consuming, as the (pronounced) coarsening stage is necessarily much longer than the growth stage.

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* On leave from the Institute of Theoretical and Experimental Physics, Moscow 117259, Russia.

- [1] M. Kardar, G. Parizi, and Y.-C. Zhang, Phys. Rev. Lett. **58**, 889 (1986).
- [2] A.-L. Barabási and H.E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge Univ. Press, Cambridge, 1995).
- [3] G.K. Batchelor, *The Theory of Homogeneous Turbulence* (Cambridge Univ. Press, Cambridge, 1956), p. 99.
- [4] G.I. Barenblatt, *Scaling, Self-similarity, and Intermediate Asymptotics* (Cambridge Univ. Press, Cambridge, 1996), p. 256.
- [5] J.D. Gunton, M. San Miguel, and P.S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J.L. Lebowitz (Academic Press, New York, 1983), Vol. 8, p. 267.
- [6] P.W. Voorhees, Annu. Rev. Mater. Sci. **22**, 197 (1992).
- [7] A.J. Bray, Adv. Phys. **43**, 357 (1994).
- [8] M. Zinke-Allmang, L.C. Feldman, and M.H. Grabow, Surface Sci. Reports **16**, 377 (1992).
- [9] J.S. Langer, Rev. Mod. Phys. **52**, 1 (1980); and in *Chance and Matter*, edited by J. Souletie, J. Vannimenus, and R. Stora (Elsevier, Amsterdam, 1987).
- [10] D.A. Kessler, J. Koplik, and H. Levine, Adv. Phys. **37**, 255 (1988).
- [11] E.A. Brener and V.I. Mel'nikov, Adv. Phys. **40**, 53 (1991).
- [12] M.B. Mineev-Weinstein, in *Fluctuations and Order. The New Synthesis* (Springer, New York, 1996), p. 239.
- [13] E. Brener, H. Müller-Krumbhaar, and D. Temkin, Phys. Rev. **54**, 2714 (1996).
- [14] H. Toyoki and K. Honda, Phys. Lett. **111**, 367 (1985).
- [15] R. Sempéré, D. Bourret, T. Woignier, J. Phalippou and R. Jullien, Phys. Rev. Lett. **71**, 3307 (1993).
- [16] W.W. Mullins and R.F. Sekerka, J. Appl. Phys. **34**, 323 (1963); **35**, 444 (1964).
- [17] I.M. Lifshitz and V.V. Slyozov, Sov. Phys. JETP **8**, 331 (1959).
- [18] For $d = 2$, the logarithmic divergence inherent in the Laplace equation should be taken care of, which does not affect the scaling exponents, similar to [26].
- [19] In doing so, we actually make a natural assumption that the function $U(\eta)$ is everywhere finite (neither zero, nor infinite).
- [20] Such a shrinkage was first predicted in Ref. [15] in the context of sintering of fractal matter.
- [21] A *perfectly* spherical (circular) shape develops if the cluster size is much smaller than the size of the system, and the noise level is negligible.
- [22] B. Meerson and P.V. Sasorov, Phys. Rev. E **53**, 3491 (1996).
- [23] P. Hohenberg and B.I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).
- [24] The case of *interface-controlled* coarsening can be more convenient for simulations, as both its sharp-interface limit (growth controlled by the difference between the mean curvature and the average of the mean curvature over the interface), and the phase-field model (a globally constrained reaction-diffusion equation exhibiting bistability) [27,22] are simpler than their counterparts in the diffusion-controlled case.
- [25] L.P. Kadanoff, J. Statist. Phys. **39**, 267 (1985).
- [26] J.A. Marqusee, J. Chem. Phys. **81**, 976 (1984).
- [27] J. Rubinstein and P. Sternberg, IMA J. Appl. Math. **48**, 249 (1992).